

The crystal structure of 3-chloro-2-(4-methylphenyl)-2H-pyrazolo[3,4-b]quinoline

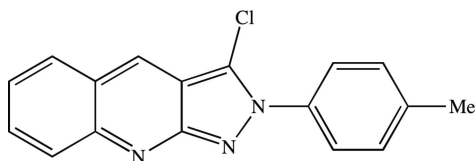
Haliwana B. V. Sowmya,^a Tholappanavara H. Suresha Kumara,^b Jerry P. Jasinski,^{c*} Sean P. Millikan,^c Hemmige S. Yathirajan^d and Christopher Glidewell^e

^aPG Department of Chemistry, Jain University, 52 Bellary Road, Hebbal, Bangalore 560 024, India, ^bUniversity B.D.T. College of Engineering, (a Constituent College of VTU, Belgaum), Davanagere 577 004, India, ^cDepartment of Chemistry, Keene State College, 229 Main Street, Keene, NH 03435-2001, USA, ^dDepartment of Studies in Chemistry, University of Mysore, Manasagangotri, Mysore 570 006, India, and ^eSchool of Chemistry, University of St Andrews, St Andrews, Fife KY16 9ST, Scotland. *Correspondence e-mail: jjasinski@keene.edu

In the molecule of 3-chloro-2-(4-methylphenyl)-2H-pyrazolo[3,4-b]quinoline, C₁₇H₁₂ClN₃, (I), the dihedral angle between the planes of the pyrazole ring and the methylated phenyl ring is 54.25 (9)°. The bond distances in the fused tricyclic system provide evidence for 10- π delocalization in the pyrazolopyridine portion of the molecule, with diene character in the fused carbocyclic ring. In the crystal, molecules of (I) are linked by two independent C—H...N hydrogen bonds, forming sheets containing centrosymmetric $R_2^2(16)$ and $R_6^4(28)$ rings, and these sheets are all linked together by π - π stacking interactions with a ring-centroid separation of 3.5891 (9) Å.

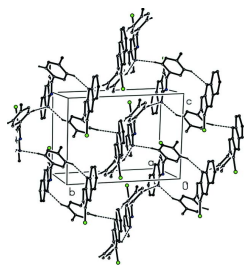
1. Chemical context

Quinoline exhibits antimalarial, anti-bacterial, antifungal, anthelmintic, cardiotoxic, anticonvulsant, anti-inflammatory and analgesic activity (Marella *et al.*, 2013). Quinoline and its fused heterocyclic derivatives constitute an important class of compounds for new drug development (Kumar *et al.*, 2009), and the medicinal applications of pyrazolo[3,4-b]quinolines have been summarized, along with an efficient synthetic method (Afghan *et al.*, 2009). Recently, we have reported the synthesis of a number of novel pyrazolo[3,4-b]quinoline derivatives, including that of the title compound (I), and molecular docking studies of their binding affinity to the active sites of human telomerase (Sowmya *et al.*, 2014). In a continuation of that study, we now report the crystal and molecular structure of one such example, the title compound 3-chloro-2-*p*-tolyl-2H-pyrazolo[3,4-b]quinoline, (I).



2. Structural commentary

Within the molecule of compound (I) (Fig. 1), the pendent phenyl group is twisted out of the plane of the fused heterocyclic ring system, as indicated by the relevant torsional angles (Table 1): the dihedral angle between the mean planes of the pyrazole and the methylated phenyl rings is 54.25 (9)°. The molecules of (I) exhibit no internal symmetry and thus they are conformationally chiral: however, the centrosymmetric



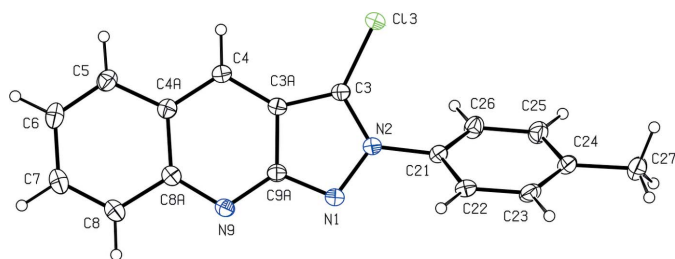


Figure 1
The molecular structure of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

space group accommodates equal numbers of both of the conformational enantiomers. The non-planar character of the molecular skeleton may be plausibly ascribed to the combined effects of the intramolecular non-bonded repulsion between the Cl substituent and the nearest H atom of the methylated phenyl ring, and of the direction-specific intermolecular interactions, in particular the hydrogen bonds.

The bond distances in compound (I) (Table 1) show some interesting features. Within the pyrazole ring, the bond distances N1—C9A and N2—C3 (Fig. 1) are identical within experimental uncertainty, although these two bonds are formally double and single bonds, respectively. In the fused carbocyclic ring, the bonds C5—C6 and C7—C8 are much shortened than any other C—C bonds in the molecule. However, in the central pyridine ring, within each of the pairs of

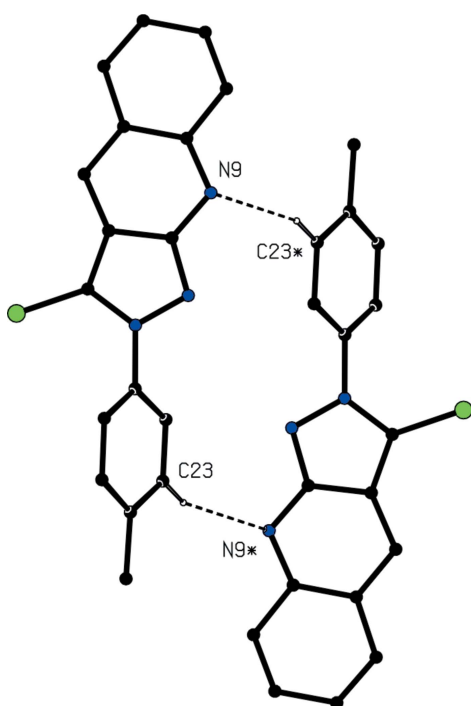


Figure 2
Part of the crystal structure of compound (I) showing the formation of a centrosymmetric hydrogen-bonded dimer. For the sake of clarity, the unit-cell outline and H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) are at the symmetry position $(-x, 1 - y, 1 - z)$.

Table 1
Selected geometric parameters (\AA , $^\circ$).

N1—N2	1.3644 (18)	C7—C8	1.358 (2)
N2—C3	1.346 (2)	C8—C8A	1.432 (2)
C3—C3A	1.398 (2)	C8A—N9	1.342 (2)
C3A—C4	1.388 (2)	N9—C9A	1.346 (2)
C4—C4A	1.394 (2)	C9A—N1	1.349 (2)
C4A—C5	1.429 (2)	C3A—C9A	1.430 (2)
C5—C6	1.357 (3)	C4A—C8A	1.446 (2)
C6—C7	1.419 (3)	C3—Cl3	1.6993 (16)
N1—N2—C21—C22	-53.7 (2)	C3—N2—C21—C22	125.08 (17)
N1—N2—C21—C26	126.42 (16)	C3—N2—C21—C26	-54.8 (2)

Table 2
Hydrogen-bond geometry (\AA , $^\circ$).

Cg1 represents the centroid of the C21—C26 ring.

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C23—H23...N9 ⁱ	0.95	2.50	3.393 (2)	157
C26—H26...N9 ⁱⁱ	0.95	2.50	3.449 (2)	174
C27—H27A...Cg1 ⁱⁱⁱ	0.98	2.84	3.653 (2)	140

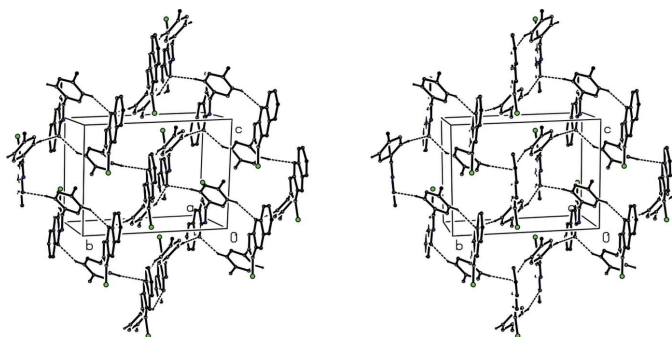
Symmetry codes: (i) $-x, -y + 1, -z + 1$; (ii) $x, -y + \frac{1}{2}, z + \frac{1}{2}$; (iii) $-x, -y + 1, -z + 2$.

corresponding bonds C3A—C4 and C4—C4A, C8A—N9 and N9—C9A, and C3A—C9A and C4A—C8A, the two distances are very similar. These observations taken together are fully consistent with a $10\text{-}\pi$ delocalized system in the pyrazolo-pyridine portion of the molecule, comparable to those found in naphthalene and azulene (Glidewell & Lloyd, 1984), while the fused carbocyclic ring has more the character of an isolated diene (*cf.* Glidewell & Lloyd, 1986).

3. Supramolecular features

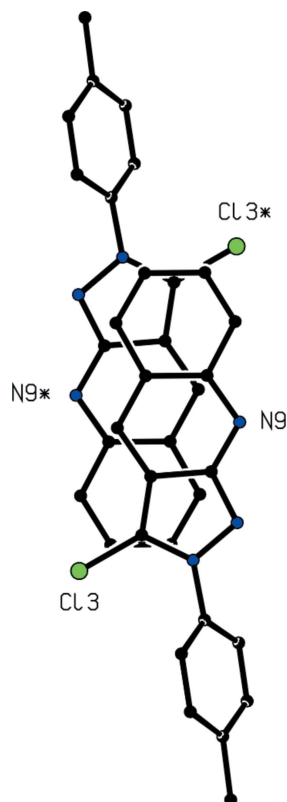
The supramolecular assembly in compound (I) is determined by two independent C—H...N hydrogen bonds (Table 2) and a $\pi\text{-}\pi$ stacking interaction, which together link the molecules into a three-dimensional framework structure. The formation of this framework is readily analysed in terms of three simpler sub-structures (Ferguson *et al.*, 1998*a,b*; Gregson *et al.*, 2000). In the simplest sub-structure, the C—H...N hydrogen bond having atom C23 as the donor links an inversion-related pair of molecules, forming a cyclic centrosymmetric dimer characterized by an $R_2^2(16)$ (Bernstein *et al.*, 1995) motif (Fig. 2), and this dimeric unit can be regarded as the basic building block in the supramolecular assembly. The second C—H...N hydrogen bond, having atom C26 as the donor, directly links the reference dimer, which is centred at $(0, \frac{1}{2}, \frac{1}{2})$ to four symmetry-related dimers centred at $(0, 0, 0)$, $(0, 1, 0)$, $(0, 0, 1)$ and $(0, 1, 1)$, thereby leading to the formation of a hydrogen-bonded sheet lying parallel to (100) , in which centrosymmetric $R_2^2(16)$ rings alternate with $R_6^4(28)$ rings (Fig. 3).

Only one hydrogen-bonded sheet passes through each unit cell, but the sheets are linked by the $\pi\text{-}\pi$ stacking interaction which is associated with the extensive overlap between the tricyclic ring systems of inversion-related pairs of molecules in


Figure 3

A stereoview of part of the crystal structure of compound (I) showing the formation of a hydrogen-bonded sheet lying parallel to (100) and containing alternating $R_2^2(16)$ and $R_6^4(28)$ rings. For the sake of clarity, H atoms not involved in the motifs shown have been omitted.

adjacent sheets (Fig. 4). The pyridine rings of the molecules at (x, y, z) and $(1 - x, 1 - y, 1 - z)$, which lie in adjacent sheets, are strictly parallel with an interplanar spacing of 3.3819 (6) Å. The ring-centroid separation is 3.5891 (9) Å, corresponding to a ring-centroid offset of *ca* 1.202 Å (Fig. 4). The effect of this interaction is to link all of the hydrogen-bonded sheets into a single three-dimensional array.


Figure 4

Part of the crystal structure of compound (I) showing the overlap of an inversion-related pair of molecules. For the sake of clarity, the unit-cell outline and all of the H atoms have been omitted. The molecules are viewed normal to the planes of the fused heterocyclic ring system and atoms marked with an asterisk (*) are at the symmetry position $(1 - x, 1 - y, 1 - z)$.

Table 3

Experimental details.

Crystal data	
Chemical formula	$C_{17}H_{12}ClN_3$
M_r	293.75
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	173
a, b, c (Å)	10.2194 (4), 13.4661 (5), 10.4600 (4)
β (°)	102.780 (4)
V (Å ³)	1403.80 (10)
Z	4
Radiation type	Cu $K\alpha$
μ (mm ⁻¹)	2.36
Crystal size (mm)	0.42 × 0.28 × 0.12
Data collection	
Diffractometer	Agilent Eos Gemini
Absorption correction	Multi-scan (<i>CrysAlis RED</i> ; Agilent, 2012)
T_{\min}, T_{\max}	0.554, 0.753
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8443, 2738, 2479
R_{int}	0.032
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.619
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.040, 0.114, 1.05
No. of reflections	2738
No. of parameters	191
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.36, -0.22

Computer programs: *CrysAlis PRO* and *CrysAlis RED* (Agilent, 2012), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015) and *PLATON* (Spek, 2009).

Despite the large number of aromatic C—H bonds in the molecule of compound (I), the only short C—H... π contact involves one of the C—H bonds of the methyl group. Not only are such bonds of low acidity but, perhaps more important, such a methyl group will be undergoing very rapid rotation about the adjacent C—C bond. When a group having local C_3 symmetry, such as a methyl group, is directly bonded to another group having local C_2 symmetry, such as a phenyl group, as in (I), the rotational barrier about the bond between them is very low, generally of the order of J mol⁻¹ rather than the usual kJ mol⁻¹ (Naylor & Wilson, 1957; Tannenbaum *et al.*, 1956). Moreover, it has been shown that simple hydrocarbyl substituents undergo rapid rotation about C—C bonds in the solid state, even at reduced temperatures (Riddell & Rogerson, 1996, 1997). Therefore, while such a C—H... π intermolecular interaction may not be regarded as structurally significant, we report it here for completeness (Table 2).

4. Database survey

Structural information on un-reduced pyrazolo[3,4-*b*]quinolines carrying a substituent at the N2 position but not at N1, is sparse. In a series of pyrazolo[3,4-*b*]quinolin-5-ones, each carrying a substituent at N2, the central heterocyclic ring is in reduced form, carrying H atoms at positions 4 and 8 (Cannon *et al.*, 2001*a,b,c,d*). By contrast, in a series of less highly reduced pyrazolo[3,4-*b*]quinolin-5-ones which each carry a substituent at N1 but not at N2, the central fused ring is fully

aromatic (Mera *et al.*, 2005; Cruz *et al.*, 2006; Portilla *et al.*, 2007). Similarly, in a series of benzo[*f*]pyrazolo[3,4-*b*]quino-
]quinolines, in each of which there is a substituent at position
1, but not at position 2, the pyridine ring is fully aromatic
(Portilla, Quiroga *et al.*, 2005; Portilla, Serrano *et al.*, 2005;
Portilla *et al.*, 2008).

5. Synthesis and crystallization

A sample of the title compound was prepared using the
recently published procedure (Sowmya *et al.*, 2014). Crystals
suitable for single-crystal X-ray diffraction were obtained by
slow evaporation, at ambient temperature and in the presence
of air, of a solution in hexane–ethyl acetate (19:1, *v/v*).

6. Refinement

Crystal data, data collection and structure refinement details
are summarized in Table 3. All H atoms were located in
difference maps, and then treated as riding atoms in geome-
trically idealized positions with C–H distances 0.95 Å
(aromatic) or 0.98 Å (methyl) and with $U_{\text{iso}}(\text{H}) = kU_{\text{eq}}(\text{C})$,
where $k = 1.5$ for the methyl group, which was permitted to
rotate but not to tilt, and 1.2 for all other H atoms.

Acknowledgements

THSK thanks the authorities of Jain University for their
support and encouragement. JPJ acknowledges the NSF–MRI
program (grant No. 1039027) for funds to purchase the X-ray
diffractometer.

References

Afghan, A., Baradarani, M. M. & Joule, J. A. (2009). *Arkivoc*, pp. 20–30.
Agilent (2012). *CrysAlis PRO* and *CrysAlis RED*. Agilent Technologies Ltd, Yarnton, England.
Bernstein, J., Davis, R. E., Shimon, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Cannon, D., Quesada, A., Quiroga, J., Mejía, D., Insuasty, B., Abonia, R., Cobo, J., Nogueras, M., Sánchez, A. & Low, J. N. (2001a). *Acta Cryst. E57*, o151–o153.

Cannon, D., Quesada, A., Quiroga, J., Mejía, D., Insuasty, B., Abonia, R., Cobo, J., Nogueras, M., Sánchez, A. & Low, J. N. (2001b). *Acta Cryst. E57*, o154–o156.
Cannon, D., Quesada, A., Quiroga, J., Mejía, D., Insuasty, B., Abonia, R., Cobo, J., Nogueras, M., Sánchez, A. & Low, J. N. (2001c). *Acta Cryst. E57*, o157–o159.
Cannon, D., Quesada, A., Quiroga, J., Mejía, D., Insuasty, B., Abonia, R., Cobo, J., Nogueras, M., Sánchez, A. & Low, J. N. (2001d). *Acta Cryst. E57*, o160–o162.
Cruz, S., Quiroga, J., de la Torre, J. M., Cobo, J., Low, J. N. & Glidewell, C. (2006). *Acta Cryst. C62*, o525–o527.
Ferguson, G., Glidewell, C., Gregson, R. M. & Meehan, P. R. (1998a). *Acta Cryst. B54*, 129–138.
Ferguson, G., Glidewell, C., Gregson, R. M. & Meehan, P. R. (1998b). *Acta Cryst. B54*, 139–150.
Glidewell, C. & Lloyd, D. (1984). *Tetrahedron*, **40**, 4455–4472.
Glidewell, C. & Lloyd, D. (1986). *J. Chem. Educ.* **63**, 306–308.
Gregson, R. M., Glidewell, C., Ferguson, G. & Lough, A. J. (2000). *Acta Cryst. B56*, 39–57.
Kumar, S., Bawa, S. & Gupta, H. (2009). *Mini Rev. Med. Chem.* **9**, 1648–1654.
Marella, A., Tanwar, O. P., Saha, R., Ali, M. R., Srivastava, S., Akhter, M., Shaquiquzaman, M. & Alam, M. M. (2013). *Saudi Pharm. J.* **21**, 1–12.
Mera, J., Quiroga, J., Cobo, J., Low, J. N. & Glidewell, C. (2005). *Acta Cryst. C61*, o442–o444.
Naylor, R. E. & Wilson, E. B. (1957). *J. Chem. Phys.* **26**, 1057–1060.
Portilla, J., Quiroga, J., Cobo, J., Low, J. N. & Glidewell, C. (2005). *Acta Cryst. C61*, o483–o489.
Portilla, J., Quiroga, J., Cobo, J., Low, J. N. & Glidewell, C. (2007). *Acta Cryst. C63*, o582–o584.
Portilla, J., Quiroga, J., Nogueras, M., de la Torre, J. M., Cobo, J., Low, J. N. & Glidewell, C. (2008). *Acta Cryst. B64*, 72–83.
Portilla, J., Serrano, H., Cobo, J., Low, J. N. & Glidewell, C. (2005). *Acta Cryst. C61*, o490–o492.
Riddell, F. G. & Rogerson, M. (1996). *J. Chem. Soc. Perkin Trans. 2*, pp. 493–504.
Riddell, F. G. & Rogerson, M. (1997). *J. Chem. Soc. Perkin Trans. 2*, pp. 249–256.
Sheldrick, G. M. (2008). *Acta Cryst. A64*, 112–122.
Sheldrick, G. M. (2015). *Acta Cryst. C71*, 3–8.
Sowmya, H. B. V., Suresha Kumara, T. H., Nagendrappa, G., Jasinski, J. P., Millikan, S. P., Chandramohan, V., Jose, G., Rashmi, S. K., Chandrika, N. & Ashwini, A. M. (2014). *J. Applicable Chem.* **3**, 2384–2392.
Spek, A. L. (2009). *Acta Cryst. D65*, 148–155.
Tannenbaum, E., Myers, R. J. & Gwinn, W. D. (1956). *J. Chem. Phys.* **25**, 42–47.

supporting information

Acta Cryst. (2015). E71, 567-570 [https://doi.org/10.1107/S205698901500818X]

The crystal structure of 3-chloro-2-(4-methylphenyl)-2H-pyrazolo[3,4-b]quinoline

Haliwana B. V. Sowmya, Tholappanavara H. Suresha Kumara, Jerry P. Jasinski, Sean P. Millikan, Hemmige S. Yathirajan and Christopher Glidewell

Computing details

Data collection: *CrysAlis PRO* (Agilent, 2012); cell refinement: *CrysAlis PRO* (Agilent, 2012); data reduction: *CrysAlis RED* (Agilent, 2012); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015) and *PLATON* (Spek, 2009).

3-Chloro-2-(4-methylphenyl)-2H-pyrazolo[3,4-b]quinoline

Crystal data

$C_{17}H_{12}ClN_3$

$M_r = 293.75$

Monoclinic, $P2_1/c$

$a = 10.2194$ (4) Å

$b = 13.4661$ (5) Å

$c = 10.4600$ (4) Å

$\beta = 102.780$ (4)°

$V = 1403.80$ (10) Å³

$Z = 4$

$F(000) = 608$

$D_x = 1.390$ Mg m⁻³

Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å

Cell parameters from 2738 reflections

$\theta = 4.4\text{--}72.6^\circ$

$\mu = 2.36$ mm⁻¹

$T = 173$ K

Block, yellow

$0.42 \times 0.28 \times 0.12$ mm

Data collection

Agilent Eos Gemini
diffractometer

Radiation source: Enhance (Cu) X-ray Source

ω scans

Absorption correction: multi-scan
(*CrysAlis RED*; Agilent, 2012)

$T_{\min} = 0.554$, $T_{\max} = 0.753$

8443 measured reflections

2738 independent reflections

2479 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.032$

$\theta_{\max} = 72.6^\circ$, $\theta_{\min} = 4.4^\circ$

$h = -12 \rightarrow 12$

$k = -12 \rightarrow 16$

$l = -12 \rightarrow 11$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.040$

$wR(F^2) = 0.114$

$S = 1.05$

2738 reflections

191 parameters

0 restraints

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0702P)^2 + 0.2814P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.36$ e Å⁻³

$\Delta\rho_{\min} = -0.22$ e Å⁻³

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.18699 (13)	0.38247 (10)	0.54035 (13)	0.0290 (3)
N2	0.21652 (13)	0.38697 (10)	0.67397 (13)	0.0269 (3)
C3	0.34907 (16)	0.38742 (11)	0.72750 (16)	0.0271 (3)
Cl3	0.41552 (4)	0.39736 (3)	0.89093 (3)	0.03435 (15)
C3A	0.41587 (16)	0.38246 (11)	0.62459 (15)	0.0257 (3)
C4	0.54815 (16)	0.37944 (11)	0.61183 (15)	0.0280 (3)
H4	0.6210	0.3825	0.6860	0.034*
C4A	0.56909 (16)	0.37163 (11)	0.48495 (16)	0.0287 (3)
C5	0.70051 (17)	0.36552 (13)	0.45927 (18)	0.0356 (4)
H5	0.7767	0.3680	0.5302	0.043*
C6	0.71795 (19)	0.35618 (14)	0.33496 (19)	0.0401 (4)
H6	0.8060	0.3516	0.3197	0.048*
C7	0.60533 (19)	0.35325 (13)	0.22768 (18)	0.0390 (4)
H7	0.6191	0.3472	0.1411	0.047*
C8	0.47823 (19)	0.35900 (12)	0.24644 (16)	0.0352 (4)
H8	0.4045	0.3569	0.1730	0.042*
C8A	0.45426 (17)	0.36816 (11)	0.37577 (15)	0.0282 (3)
N9	0.32609 (13)	0.37210 (10)	0.38697 (13)	0.0283 (3)
C9A	0.30883 (16)	0.37944 (11)	0.51055 (15)	0.0264 (3)
C21	0.10959 (16)	0.39242 (12)	0.74232 (16)	0.0283 (3)
C22	0.01295 (16)	0.46631 (12)	0.70896 (16)	0.0318 (3)
H22	0.0147	0.5109	0.6390	0.038*
C23	-0.08594 (16)	0.47332 (13)	0.78014 (17)	0.0356 (4)
H23	-0.1520	0.5239	0.7588	0.043*
C24	-0.09102 (16)	0.40803 (14)	0.88226 (17)	0.0353 (4)
C25	0.00467 (17)	0.33313 (14)	0.90984 (18)	0.0393 (4)
H25	0.0016	0.2870	0.9779	0.047*
C26	0.10438 (17)	0.32453 (13)	0.83996 (17)	0.0360 (4)
H26	0.1685	0.2725	0.8590	0.043*
C27	-0.19679 (19)	0.41851 (18)	0.9614 (2)	0.0476 (5)
H27A	-0.1545	0.4387	1.0510	0.071*
H27B	-0.2424	0.3547	0.9636	0.071*
H27C	-0.2623	0.4689	0.9212	0.071*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0265 (7)	0.0343 (7)	0.0250 (7)	-0.0008 (5)	0.0028 (5)	-0.0009 (5)
N2	0.0244 (7)	0.0303 (7)	0.0251 (7)	0.0004 (5)	0.0035 (5)	-0.0002 (5)

C3	0.0251 (8)	0.0298 (8)	0.0251 (8)	0.0001 (6)	0.0026 (6)	-0.0006 (6)
Cl3	0.0305 (2)	0.0482 (3)	0.0228 (2)	0.00019 (15)	0.00256 (16)	-0.00138 (14)
C3A	0.0272 (8)	0.0244 (7)	0.0243 (8)	-0.0007 (5)	0.0034 (6)	-0.0001 (6)
C4	0.0261 (8)	0.0288 (7)	0.0278 (8)	-0.0013 (6)	0.0033 (6)	-0.0009 (6)
C4A	0.0298 (8)	0.0243 (7)	0.0322 (8)	-0.0025 (6)	0.0074 (7)	-0.0008 (6)
C5	0.0304 (9)	0.0361 (9)	0.0411 (9)	-0.0026 (7)	0.0093 (7)	-0.0028 (7)
C6	0.0366 (9)	0.0391 (9)	0.0503 (11)	-0.0026 (7)	0.0220 (8)	-0.0036 (8)
C7	0.0500 (11)	0.0363 (9)	0.0359 (9)	-0.0041 (8)	0.0204 (8)	-0.0028 (7)
C8	0.0445 (10)	0.0335 (9)	0.0288 (8)	-0.0032 (7)	0.0109 (7)	-0.0009 (7)
C8A	0.0336 (8)	0.0226 (7)	0.0287 (8)	-0.0014 (6)	0.0078 (6)	0.0003 (6)
N9	0.0306 (7)	0.0293 (7)	0.0243 (7)	-0.0020 (5)	0.0042 (5)	-0.0003 (5)
C9A	0.0270 (8)	0.0246 (7)	0.0267 (8)	-0.0008 (6)	0.0038 (6)	-0.0002 (6)
C21	0.0230 (7)	0.0330 (8)	0.0283 (8)	0.0005 (6)	0.0045 (6)	-0.0020 (6)
C22	0.0266 (8)	0.0352 (8)	0.0305 (8)	0.0015 (6)	-0.0003 (6)	0.0016 (7)
C23	0.0230 (8)	0.0413 (9)	0.0397 (9)	0.0047 (6)	0.0005 (7)	-0.0042 (7)
C24	0.0236 (8)	0.0463 (10)	0.0355 (9)	-0.0018 (6)	0.0053 (7)	-0.0075 (7)
C25	0.0320 (9)	0.0486 (10)	0.0388 (9)	0.0009 (7)	0.0111 (7)	0.0095 (8)
C26	0.0300 (8)	0.0378 (9)	0.0418 (10)	0.0067 (7)	0.0114 (7)	0.0084 (7)
C27	0.0302 (9)	0.0671 (13)	0.0483 (11)	-0.0017 (8)	0.0145 (8)	-0.0121 (10)

Geometric parameters (Å, °)

N1—N2	1.3644 (18)	C7—H7	0.9500
N2—C3	1.346 (2)	C8—H8	0.9500
C3—C3A	1.398 (2)	N2—C21	1.434 (2)
C3A—C4	1.388 (2)	C3—Cl3	1.6993 (16)
C4—C4A	1.394 (2)	C21—C26	1.380 (2)
C4A—C5	1.429 (2)	C21—C22	1.391 (2)
C5—C6	1.357 (3)	C22—C23	1.385 (2)
C6—C7	1.419 (3)	C22—H22	0.9500
C7—C8	1.358 (2)	C23—C24	1.393 (3)
C8—C8A	1.432 (2)	C23—H23	0.9500
C8A—N9	1.342 (2)	C24—C25	1.390 (3)
N9—C9A	1.346 (2)	C24—C27	1.507 (2)
C9A—N1	1.349 (2)	C25—C26	1.384 (2)
C3A—C9A	1.430 (2)	C25—H25	0.9500
C4A—C8A	1.446 (2)	C26—H26	0.9500
C4—H4	0.9500	C27—H27A	0.9800
C5—H5	0.9500	C27—H27B	0.9800
C6—H6	0.9500	C27—H27C	0.9800
C9A—N1—N2	103.40 (12)	C8—C8A—C4A	118.05 (15)
C3—N2—N1	113.60 (13)	C8A—N9—C9A	115.12 (14)
C3—N2—C21	126.87 (14)	N9—C9A—N1	123.20 (14)
N1—N2—C21	119.52 (12)	N9—C9A—C3A	124.38 (14)
N2—C3—C3A	107.30 (14)	N1—C9A—C3A	112.41 (14)
N2—C3—Cl3	124.06 (12)	C26—C21—C22	121.19 (15)
C3A—C3—Cl3	128.59 (13)	C26—C21—N2	119.56 (14)

C4—C3A—C3	136.66 (15)	C22—C21—N2	119.25 (14)
C4—C3A—C9A	120.04 (14)	C23—C22—C21	118.42 (16)
C3—C3A—C9A	103.30 (14)	C23—C22—H22	120.8
C3A—C4—C4A	116.84 (15)	C21—C22—H22	120.8
C3A—C4—H4	121.6	C22—C23—C24	121.64 (15)
C4A—C4—H4	121.6	C22—C23—H23	119.2
C4—C4A—C5	122.13 (16)	C24—C23—H23	119.2
C4—C4A—C8A	119.06 (15)	C25—C24—C23	118.24 (15)
C5—C4A—C8A	118.81 (15)	C25—C24—C27	120.74 (17)
C6—C5—C4A	120.91 (17)	C23—C24—C27	121.02 (17)
C6—C5—H5	119.5	C26—C25—C24	121.16 (16)
C4A—C5—H5	119.5	C26—C25—H25	119.4
C5—C6—C7	120.32 (17)	C24—C25—H25	119.4
C5—C6—H6	119.8	C21—C26—C25	119.26 (16)
C7—C6—H6	119.8	C21—C26—H26	120.4
C8—C7—C6	121.22 (16)	C25—C26—H26	120.4
C8—C7—H7	119.4	C24—C27—H27A	109.5
C6—C7—H7	119.4	C24—C27—H27B	109.5
C7—C8—C8A	120.68 (17)	H27A—C27—H27B	109.5
C7—C8—H8	119.7	C24—C27—H27C	109.5
C8A—C8—H8	119.7	H27A—C27—H27C	109.5
N9—C8A—C8	117.40 (15)	H27B—C27—H27C	109.5
N9—C8A—C4A	124.55 (14)		
C9A—N1—N2—C3	0.34 (16)	C8—C8A—N9—C9A	179.20 (14)
C9A—N1—N2—C21	179.24 (13)	C4A—C8A—N9—C9A	-0.2 (2)
N1—N2—C3—C3A	-0.29 (17)	C8A—N9—C9A—N1	-178.78 (14)
C21—N2—C3—C3A	-179.08 (14)	C8A—N9—C9A—C3A	-0.4 (2)
N1—N2—C3—Cl3	177.38 (11)	N2—N1—C9A—N9	178.30 (14)
C21—N2—C3—Cl3	-1.4 (2)	N2—N1—C9A—C3A	-0.27 (16)
N2—C3—C3A—C4	-179.33 (17)	C4—C3A—C9A—N9	1.1 (2)
Cl3—C3—C3A—C4	3.1 (3)	C3—C3A—C9A—N9	-178.44 (14)
N2—C3—C3A—C9A	0.10 (16)	C4—C3A—C9A—N1	179.66 (14)
Cl3—C3—C3A—C9A	-177.43 (12)	C3—C3A—C9A—N1	0.11 (17)
C3—C3A—C4—C4A	178.21 (17)	N1—N2—C21—C22	-53.7 (2)
C9A—C3A—C4—C4A	-1.1 (2)	N1—N2—C21—C26	126.42 (16)
C3A—C4—C4A—C5	-178.51 (14)	C3—N2—C21—C22	125.08 (17)
C3A—C4—C4A—C8A	0.6 (2)	C3—N2—C21—C26	-54.8 (2)
C4—C4A—C5—C6	178.81 (16)	C26—C21—C22—C23	2.9 (2)
C8A—C4A—C5—C6	-0.3 (2)	N2—C21—C22—C23	-177.01 (14)
C4A—C5—C6—C7	0.6 (3)	C21—C22—C23—C24	-0.6 (3)
C5—C6—C7—C8	-0.4 (3)	C22—C23—C24—C25	-1.5 (3)
C6—C7—C8—C8A	0.0 (3)	C22—C23—C24—C27	178.15 (16)
C7—C8—C8A—N9	-179.12 (15)	C23—C24—C25—C26	1.4 (3)
C7—C8—C8A—C4A	0.3 (2)	C27—C24—C25—C26	-178.25 (17)
C4—C4A—C8A—N9	0.1 (2)	C22—C21—C26—C25	-3.0 (3)
C5—C4A—C8A—N9	179.25 (14)	N2—C21—C26—C25	176.89 (16)
C4—C4A—C8A—C8	-179.31 (14)	C24—C25—C26—C21	0.8 (3)

C5—C4A—C8A—C8 -0.2 (2)

Hydrogen-bond geometry (Å, °)

Cg1 represents the centroid of the C21–C26 ring.

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
C23—H23 \cdots N9 ⁱ	0.95	2.50	3.393 (2)	157
C26—H26 \cdots N9 ⁱⁱ	0.95	2.50	3.449 (2)	174
C27—H27A \cdots Cg1 ⁱⁱⁱ	0.98	2.84	3.653 (2)	140

Symmetry codes: (i) $-x, -y+1, -z+1$; (ii) $x, -y+1/2, z+1/2$; (iii) $-x, -y+1, -z+2$.